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CHEMICALLY RESISTANT COATING FOR SILICATE GLASS PROTECTION

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Based on metaphosphate compositions and boron orthophosphate, multicomponent phosphate glasses were developed which exhibit high resistance to hydrofluoric acid, have a TCLE of $(72...92) \times 10^{-7}\,K^{-1}$ and a softening temperature of 435 – 590°C, and can be used in the production of a phosphate film coating for the surface of sheet silicate glass, in order to protect it from the effect of hydrofluoric acid.

The purpose of the present study was to develop multicomponent phosphate compositions resistant to hydrofluoric acid and suitable for deposition in the form of a coating on sheet silicate glass to protect it from the effect of hydrofluoric acid solution and vapor.

Since such chemically resistant phosphate glass is intended to develop a thin-layer coat on a window pane surface, the developed composition should be relatively low-melting and possess a TCLE close to the TCLE of window glass. The first condition must be satisfied in order to form the coating film within a temperature interval in which the deformation of the substrate can be avoided, and the second one should provide for the consistency of the film with the substrate material and the absence of stresses.

Silicate window glass has the following thermophysical parameters: TCLE $90 \times 10^{-7}\,K^{-1}$, vitrification temperature $t_g \cong 550$°C, and softening temperature $t_f \cong 600$°C.

The results of the earlier studies [1, 2] indicated that the main component of chemically resistant glass should be aluminum metaphosphate with boron orthophosphate additives, since aluminophosphate and aluminoboron phosphate glasses are the most resistant not only to hydrofluoric acid, but to aqueous media as well, which is important for their practical application. However, pure aluminophosphate glass and aluminoboron phosphate glasses are high-melting. The softening temperature of aluminoboron phosphate glasses, which are resistant to hydrofluoric acid, lies within the interval of 700 – 770°C. These glasses are also characterized by low TCLE: $54 \times 10^{-7}\,K^{-1}$ (aluminum metaphosphate), $(40...60) \times 10^{-7}\,K^{-1}$ (aluminoboron phosphate glasses), i.e., 1.5 – 2 times lower than the TCLE of window glass.

In order to decrease the melting temperature and increase the TCLE of such glasses, it is advisable to introduce certain quantities of alkali metaphosphates to their compositions. Although alkali metaphosphate glasses are chemically unstable, in combination with boron orthophosphate, their resistance can be significantly increased [1, 2].

The compositions were developed following the I. D. Tykachinskii method [3], according to which the properties of compound mixtures are determined based on the component fractions. Considering the preset TCLE value $(90 \times 10^{-7}\,K^{-1})$, the fractional part of simple binary metaphosphates was calculated for a composition consisting of two metaphosphates. Property data supplied in [1, 2] were used in the calculation. The metaphospate pairs were selected in such a way that one of them has a TCLE up to $90 \times 10^{-7}\,K^{-1}$ ($Al(PO_3)_3$, $Zn(PO_3)_2$, $Cu(PO_3)_2$, etc.), while the other member of the pair has a TCLE of more than $90 \times 10^{-7}\,K^{-1}$ ($LiPO_3$, $NaPO_3$, KPO_3, $Ba(PO_3)_2$, etc.). The softening temperature was estimated for the designed compositions. The calculations were carried out on a computer. The calculation results are given in Table 1.

Some of the designed glass compositions were melted in an electrical furnace with silite heaters in corundum crucibles of 0.3 liter capacity using metaphosphates of "pure" grade as materials. Melting was carried out according to the accepted method, which involves casting melted glass on a metal plate and subsequent annealing. The glasses were subjected to chemical analysis, and their thermal properties were determined. Table 2 presents the results of the chemical analysis and the estimated and experimental data on the thermal properties of the synthesized glasses. A comparison of all data indicated that the discrepancies between the estimated and the experimental values of t_f and TCLE do not exceed 10 – 15%, if the deviation in the composition does not exceed 3 – 4%. More significant discrepancies between the estimated and the experimental data are related to substantial modifications of the composition in the course of synthesis.

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Based on the estimated compositions of ternary metaphosphate glasses, we prepared more complex mixtures, so that t_f of the mixture does not exceed 500°C. To make up batches, we selected the lowest-melting metaphosphate glasses which contained components resistant to hydrofluoric acid: $0.54Al(PO_3)_3 - 0.46LiPO_3$ (t_f = 581°C), $0.7Zn(PO_3)_2 - 0.3LiPO_3$ (t_f = 431°C), $0.88Cu(PO_3)_2 - 0.12LiPO_3$ (t_f = 414°C). The mixture compositions were calculated for the preset values of t_f: 475, 450, and 462.5°C.

Additives of 10 – 20% BPO_4 were introduced by means of partial replacement of one or several batch components. An additional quantity of $Al(PO_3)_3$, i.e., 20 – 30% above the estimated content, was added to some mixtures to provide for better chemical resistance. The developed compositions are listed in Table 3 converted to the molar content of oxides.

The glasses of the designed compositions were melted in a gas-heated crucible furnace in corundum crucibles of 0.5 liter capacity at 1200 – 1400°C. The exposure at the maximum temperature was 40 – 60 min.

TABLE 1

System	Fractional part factors	Softening temperature (fractional), °C	Molar content in glass, %
$Al(PO_3)_3 - KPO_3$	0.81 – 0.19	659.78	71.00 P_2O_5, 5.50 K_2O, 23.50 Al_2O_3
$Al(PO_3)_3 - NaPO_3$	0.73 – 0.27	628.89	71.00 P_2O_5, 8.00 Na_2O, 21.00 Al_2O_3
$Al(PO_3)_3 - LiPO_3$	0.56 – 0.44	581.60	81.00 P_2O_5, 3.50 Li_2O, 15.40 Al_2O_3
$Al(PO_3)_3 - Ba(PO_3)_2$	0.07 – 0.93	523.92	51.85 P_2O_5, 46.31 BaO, 1.85 Al_2O_3
$Al(PO_3)_3 - Sr(PO_3)_2$	0.32 – 0.68	595.40	57.96 P_2O_5, 34.07 SrO, 7.96 Al_2O_3
$Ga(PO_3)_3 - KPO_3$	0.91 – 0.09	615.59	72.76 P_2O_5, 4.49 K_2O, 22.76 Ga_2O_3
$Ga(PO_3)_3 - NaPO_3$	0.87 – 0.13	600.47	71.70 P_2O_5, 6.60 Na_2O, 21.70 Ga_2O_3
$Ga(PO_3)_3 - LiPO_3$	0.76 – 0.24	559.92	69.08 P_2O_5, 11.83 Li_2O, 19.08 Ga_2O_3
$Ga(PO_3)_3 - Ba(PO_3)_2$	0.58 – 0.42	577.50	64.52 P_2O_5, 20.96 BaO, 14.52 Ga_2O_3
$Ga(PO_3)_3 - Sr(PO_3)_2$	0.65 – 0.35	590.45	66.18 P_2O_5, 17.64 SrO, 16.18 Ga_2O_3
$Ga(PO_3)_3 - Ca(PO_3)_2$	0.48 – 0.52	603.00	61.91 P_2O_5, 26.17 CaO, 11.91 Ga_2O_3
$Mg(PO_3)_2 - KPO_3$	0.91 – 0.09	516.61	50.00 P_2O_5, 4.52 K_2O, 45.48 MgO
$Mg(PO_3)_2 - NaPO_3$	0.86 – 0.14	549.36	50.00 P_2O_5, 6.94 Na_2O, 43.06 MgO
$Mg(PO_3)_2 - LiPO_3$	0.74 – 0.26	531.82	50.00 P_2O_5, 13.01 Li_2O, 36.99 MgO
$Mg(PO_3)_2 - Ba(PO_3)_2$	0.55 – 0.45	546.05	50.00 P_2O_5, 27.72 BaO, 22.28 MgO
$Mg(PO_3)_2 - Sr(PO_3)_2$	0.58 – 0.42	562.24	50.00 P_2O_5, 21.03 SrO, 28.97 MgO
$Zn(PO_3)_2 - KPO_3$	0.88 – 0.12	436.08	50.00 P_2O_5, 5.93 K_2O, 44.07 ZnO
$Zn(PO_3)_2 - NaPO_3$	0.83 – 0.17	431.08	50.00 P_2O_5, 8.66 Na_2O, 41.34 ZnO
$Zn(PO_3)_2 - LiPO_3$	0.70 – 0.30	431.10	50.00 P_2O_5, 15.16 Li_2O, 34.84 ZnO
$Zn(PO_3)_2 - Ba(PO_3)_2$	0.43 – 0.57	488.37	50.00 P_2O_5, 28.56 BaO, 21.44 ZnO
$Zn(PO_3)_2 - Sr(PO_3)_2$	0.68 – 0.32	453.74	50.00 P_2O_5, 19.12 SrO, 30.88 ZnO
$Zn(PO_3)_2 - Ca(PO_3)_2$	0.36 – 0.64	525.80	50.00 P_2O_5, 31.78 CaO, 18.22 ZnO
$Cu(PO_3)_2 - Pb(PO_3)_2$	0.64 – 0.36	396.08	50.00 P_2O_5, 17.91 PbO, 32.09 CuO
$Cu(PO_3)_2 - KPO_3$	0.96 – 0.04	414.08	50.00 P_2O_5, 1.98 K_2O, 48.02 CuO
$Cu(PO_3)_2 - NaPO_3$	0.94 – 0.06	412.82	50.00 P_2O_5, 3.14 Na_2O, 46.86 CuO
$Cu(PO_3)_2 - LiPO_3$	0.88 – 0.12	413.60	50.00 P_2O_5, 6.13 Li_2O, 43.87 CuO
$Cu(PO_3)_2 - Ba(PO_3)_2$	0.79 – 0.21	439.64	50.00 P_2O_5, 10.29 BaO, 39.71 CuO
$Cu(PO_3)_2 - Sr(PO_3)_2$	0.81 – 0.19	440.05	50.00 P_2O_5, 9.26 SrO, 40.74 CuO
$Cu(PO_3)_2 - Ca(PO_3)_2$	0.65 – 0.35	470.30	50.00 P_2O_5, 17.31 CaO, 32.69 CuO

TABLE 2

Estimated glass composition in metaphospate fractions	Estimated glass composition in oxides, %		Glass composition by chemical analysis, molar content, %	Properties			
				estimated		experimental	
	molar content	weight content		softening temperature, °C	TCLE, 10^{-7} K^{-1}	softening temperature, °C	TCLE, 10^{-7} K^{-1}
$0.44LiPO_3 - 0.56Al(PO_3)_3$	68.00 P_2O_5 14.00 Li_2O 18.00 Al_2O_3	81.08 P_2O_5 3.52 Li_2O 15.40 Al_2O_3	77.33 P_2O_5 3.62 Li_2O 19.05 Al_2O_3	581	90	530	80
$0.27NaPO_3 - 0.73Al(PO_3)_3$	71.00 P_2O_5 8.00 Na_2O 21.00 Al_2O_3	79.26 P_2O_5 3.89 Na_2O 16.83 Al_2O_3	75.72 P_2O_5 3.80 Na_2O 20.48 Al_2O_3	629	90	637	87
$0.19KPO_3 - 0.81Al(PO_3)_3$	71.00 P_2O_5 5.50 K_2O 23.50 Al_2O_3	77.60 P_2O_5 4.00 K_2O 18.40 Al_2O_3	70.06 P_2O_5 5.14 K_2O 24.80 Al_2O_3	660	90	673	71
$0.57Ba(PO_3)_3 - 0.43Zn(PO_3)_2$	50.00 P_2O_5 28.56 BaO 0 Al_2O_3 21.44 ZnO	53.78 P_2O_5 33.10 BaO 0 Al_2O_3 13.18 ZnO	53.30 P_2O_5 32.30 BaO 1.00 Al_2O_3 14.40 ZnO	488	90	491	94
$0.07Al(PO_3)_3 - 0.93Ba(PO_3)_3$	51.85 P_2O_5 1.85 Al_2O_3 46.30 BaO	50.30 P_2O_5 1.28 Al_2O_3 48.42 BaO	48.10 P_2O_5 2.98 Al_2O_3 48.92 BaO	524	90	532	84
$0.91Mg(PO_3)_3 - 0.09KPO_3$	50.00 P_2O_5 45.50 MgO 4.50 K_2O 0 Al_2O_3	76.00 P_2O_5 19.47 MgO 4.53 K_2O 0 Al_2O_3	73.90 P_2O_5 19.57 MgO 4.90 K_2O 1.63 Al_2O_3	517	90	516	92

TABLE 3

Glass composition in metaphosphates	Molar content, %						Properties				
							estimated		experimental		
	P_2O_5	Al_2O_3	Li_2O	ZnO	CuO	B_2O_3	TCLE, 10^{-7} K^{-1}	softening temperature, °C	TCLE, 10^{-7} K^{-1}	softening temperature, °C	weight loss in hydrofluoric acid, mg/cm^2
$7Al(PO_3)_3 - 32Li_2O - 61Zn(PO_3)_2$	52.0	3.0	10.0	35.0	–	–	90	450	79	440	0.360
$12Al(PO_3)_3 - 20LiPO_3 - 68Cu(PO_3)_2$	53.5	3.5	6.0	–	37.0	–	90	450	85	438	0.210
$10Al(PO_3)_3 - 25LiPO_3 - 30Zn(PO_3)_2 - 35Cu(PO_3)_2$	55.0	5.0	7.0	15.0	18.0	–	90	450	83	446	0.290
$10Al(PO_3)_3 - 25LiPO_3 - 30Zn(PO_3)_2 - 25Cu(PO_3)_2 - 10BPO_4$	53.0	3.0	7.0	19.0	15.0	3.0	–	–	88	452	0.110
$10Al(PO_3)_3 - 25LiPO_3 - 20Zn(PO_3)_2 - 35Cu(PO_3)_2 - 10BPO_4$	53.0	3.0	7.0	13.0	21.0	3.0	–	–	96	437	0.120
$10Al(PO_3)_3 - 15LiPO_3 - 30Zn(PO_3)_2 - 35Cu(PO_3)_2 - 10BPO_4$	55.0	5.0	4.0	16.0	17.0	3.0	–	–	79	460	0.080
$9Al(PO_3)_3 - 23LiPO_3 - 27Zn(PO_3)_2 - 32Cu(PO_3)_2 - 10BPO_4$	58.0	2.5	5.0	15.0	17.0	2.5	–	–	84	448	0.094
$10Al(PO_3)_3 - 20LiPO_3 - 25Zn(PO_3)_2 - 30Cu(PO_3)_2 - 15BPO_4$	55.0	5.5	5.5	13.5	16.5	4.0	–	–	73	449	0.010
$28Al(PO_3)_3 - 16LiPO_3 - 20Zn(PO_3)_2 - 24Cu(PO_3)_2 - 12BPO_4$	58.0	8.0	4.5	12.0	14.0	3.5	–	–	92	435	0.006
$40Al(PO_3)_2 - 13LiPO_3 - 17Zn(PO_3)_2 - 20Cu(PO_3)_2 - 10BPO_4$	61.0	11.0	3.0	9.0	11.0	5.0	–	–	82	465	0.026
$16Al(PO_3)_3 - 35LiPO_3 - 49Zn(PO_3)_2$	55.0	5.0	10.0	30.0	–	–	90	475	85	470	0.063
$21Al(PO_3)_3 - 24LiPO_3 - 55Cu(PO_3)_2$	56.0	6.0	7.0	–	31.0	–	90	475	82	473	0.044
$19Al(PO_3)_3 - 29LiPO_3 - 25Zn(PO_3)_2 - 27Cu(PO_3)_2$	56.0	6.0	8.0	15.0	15.0	–	90	475	87	480	0.051
$19Al(PO_3)_2 - 19LiPO_3 - 25Zn(PO_3)_2 - 17Cu(PO_3)_2 - 10BPO_4$	57.0	6.0	9.0	16.0	9.0	3.0	–	–	77	472	0.028
$19Al(PO_3)_3 - 29LiPO_3 - 15Zn(PO_3)_2 - 27Cu(PO_3)_2 - 10BPO_4$	57.0	6.0	9.0	9.0	16.0	3.0	–	–	89	487	0.031
$19Al(PO_3)_3 - 19LiPO_3 - 25Zn(PO_3)_2 - 27Cu(PO_3)_2 - 10BPO_4$	57.0	6.0	6.0	14.0	14.0	3.0	–	–	86	474	0.029
$17Al(PO_3)_3 - 25LiPO_3 - 20Zn(PO_3)_2 - 21Cu(PO_3)_2 - 17BPO_4$	55.0	5.0	8.0	13.0	14.0	5.0	–	–	78	509	0.014
$45Al(PO_3)_3 - 16LiPO_3 - 13Zn(PO_3)_2 - 14Cu(PO_3)_2 - 11BPO_4$	63.0	13.0	5.0	8.0	8.0	3.0	–	–	72	485	0.024

It can be seen from the data in Table 3 that the introduction of 10 – 20% BPO_4 to the multicomponent compositions improves their chemical resistance and does not significantly increase the t_f of glasses.

The performed experiments made it possible to select the optimum compositions which have high resistance to hydrofluoric acid, a TCLE equal to $(72...92) \times 10^{-7}$ K^{-1} and a softening temperature of 435 – 509°C. The weight losses of these glasses after 24 h treatment in hydrofluoric acid at room temperature did not exceed 0.67 mg/cm^2. The glass composition is (wt.%): 76.80 P_2O_5, 4.60 – 13.90 Al_2O_3, 3.60 – 9.40 ZnO, 0.35 – 1.05 Li_2O, 1.30 – 3.90 B_2O_3, 3.20 – 14.00 CuO (USSR Inv. Certif. No. 1346598).

Multicomponent glasses of the optimum compositions were used to produce phosphate film coatings on the surface of grade M_1 sheet silicate glass by means of the fusion of the finely disperse fraction.

The glasses were crushed to a particle size of 1 – 3 μm; after that alcohol suspension was prepared and deposited on degreased window glass plates and dried at 50 – 70°C for 10 – 20 min. Then the plates were heated at 300 – 350°C for 1 h for more complete removal of the adsorbed water. Heat treatment was performed at 550 – 580°C for 15 – 20 min up to complete phosphate glass fusion; next, annealing was carried out by a gradual temperature decrease to 100 – 150°C. In this way, homogenous transparent coatings 5 – 25 μm thick were obtained.

The coatings were tested for resistance to hydrofluoric acid. For this purpose, plates with film coatings were heated to approximately 35°C and placed on the bottom of a paraffin vessel, so that all the facets of the plate except for the coated surface were covered with melted paraffin. After that, 40%-solution of hydrofluoric acid was poured into the vessel and held for 1 h, after which the acid was removed, the ves-

sel was washed with distilled water, and the plate was extracted, washed again with water and alcohol, and dried. By weighing the plate before and after pickling, it was possible to determine the weight loss per surface area unit. A reference plate without a protective coat was treated in exactly the same way.

The experiments demonstrate that the phosphate film possesses protective properties and decreases the weight losses by a factor of 70 – 100. The weight losses in the reference window glass plates amount to 70.9 – 73.8 mg/cm^2, and an opaque loose crust is formed on the glass surface, which comes off in drying. The glass surface becomes frosted and exhibits stellar-shaped etched patterns. When the plates with the coatings were treated in the same way, it was found that the weight losses amounted to 0.7 – 0.8 mg/cm^2 and high clarity of the glass was preserved.

The proposed method for the protection of sheet silicate glass is promising and can be used in glazing of exhaust hoods in industrial and laboratory premises where hydrofluoric acid solutions are used, in particular, in chemical polishing of cut crystal products. It is well known that the window-panes in such interiors quickly become opaque, which degrades the comfort level and the illumination intensity of such working places.

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